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Corrosion Inhibitory Effects of a New Synthetic Symmetrical Schiff-Base on Mild Steel in Acid Media

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In this investigation the inhibitory effect of a new synthesized tetradentate Schiff-base bis(2-hydroxy-1-naphthaldehyde) 1,6-hexadiamine (A1) on the corrosion of mild steel in 1 M HCl and 0.5 M H_2SO_4 media solutions was studied using various techniques including electrochemical impedance spectroscopy (EIS) polarization curves and weight loss. This compound is a very good inhibitor and has a better behaviour in 1 M HCl than 0.5 H_2SO_4. A potentiodynamic polarization study shows this inhibitor has cathodic and anodic nature. Changes in Tafel and impedance parameters I_{corr}, R_{ct} & C_{dl} indicate that the absorbed protective film grows with increasing exposure time and concentration of inhibitor. Maximum inhibition efficiency reached was about 97% and 95% at 100 ppm (A1) in 1 M HCl and 0.5 M H_2SO_4. The adsorption of this inhibitor on mild steel surface in both acidic media follows a Langmuir adsorption isotherm.

Key Words: Inhibitor, Electrochemical behaviour, Mild steel, Langmuir, Polarization.

INTRODUCTION

Ferrous metals and their alloys are extensively used in industry. Metals, which are subjected to use must have a clean surface free from salt or oxide scale. To remove unwanted scale such as mill scale rust, metal is immersed in an acid solution known as an acid pickling bath. After the scale is dissolved, the acid may attack the metal. In order to reduce the metal attack and consumption of the acid, corrosion inhibitors are added to the pickling solution. Hydrochloric and sulfuric acids are the most commonly used acids in the pickling bath[1]. The largest class of inhibitors are adsorption type inhibitors. In general these are organic compounds, which adsorb on the metal surface and suppress metal dissolution and reduction reactions[2]. In many cases, the role of inhibitors is to form a surface coating one or several molecular layers thick that serves as a barrier[3]. To acid attack chemisorption is probably the most important type of interaction between the metal surface and an inhibitor molecule[1]. Typical of this class of inhibitors are the organic amines[2]. Schiff bases—the condensation products of an amine and a ketone or aldehyde, and with $R_2C{=}NR$, are examples of this category. In

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addition the Schiff base synthesis is simple and can easily introduce substituent to produce promising inhibitors. We have studied the electronic properties of Schiff-base compound **(A1)** (Fig. 1) by using a semi-empirical method by MOPAC package[5]. This program can be used to study the electronic structure and energies of ground state and excited state of molecules, such as hyperpolarizability (β) and second hyperpolarizability (γ).

Semi-empirical molecular orbital calculations have been performed on symmetric Schiff-base ligand. The effected corrosion inhibitor on mild steel and theoretical study of the molecular properties of this compound by using MOPAC 6.0 program package have been done. Recently we have reported some quantum chemical calculations by using MOPAC 6.0 program[6, 7]. In this report the properties of the electronic structure and symmetry of the MO levels for **A1** Schiff base compound as corrosion inhibitor for mild steel in 1.0 M HCl and 0.5 M H_2SO_4 media have been calculated .

The present paper studied the inhibiting effect of a newly synthesized Schiff base **(A1)** on the corrosion of mild steel in 0.5 M H_2SO_4 and 1 M HCl solutions were evaluated by various techniques including electrochemical impedance spectroscopy (EIS), polarization and weight loss method.

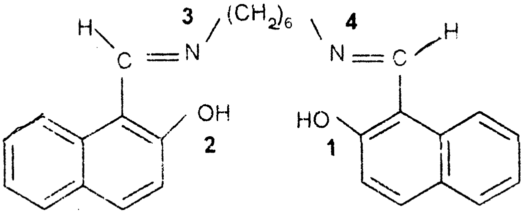


Fig. 1. Structure of Schiff base compound (A1)

EXPERIMENTAL

All precursor chemicals were of analytical reagent grade Merck or Fluka and were used without further purification.

The condensation product of an amine with a ketone or aldehyde with $R_2C{=}NR'$ as general formula are the known examples of this category and have been investigated for the inhibition of acid corrosion of mild steel[8, 9]. Schiff-base ligand was prepared in high yields (75%) *via* condensation of ethanolic solutions of aromatic aldehydes with 1,6-hexane diamine[10]. Microanalyses (C, H and N) were performed on a Perkin-Elmer analyzer, UV-Vis spectra were recorded in dimethyl formamide (DMF) with a Beckman DU-7000 spectrometer, and λ_{max} values were accurate to 0.1 nm. Infrared spectra were recorded as Nujol mulls using a Shimadzu DR-8001 FT-IR instrument. Also, the structure of this Schiff-base ligand was confirmed by using ^{1}H-NMR and ^{13}C-NMR spectroscopy, and mass spectrometry.

Samples and solutions: In this study, mild steel specimens containing (in wt %) 0.09% P, 0.30% Si, 0.07% Mn, 0.03% Al, 0.20% C, and the remainder Iron were used for the gravimetric and electrochemical measurements. The surface of specimens was mechanically polished on wet SiC abrasive paper (grade 120-600-1200), rinsed with distilled water, degreased with absolute ethanol and dried at room temperature before use. All materials used were extra pure and solutions were prepared by using distilled water. The concentration range of inhibitor employed was 25–100 ppm in both acids.

Gravimetric and electrochemical measurements: The specimens used for gravimetric measurements had a rectangular form (1 cm × 1 cm × 0.1 cm). The weight loss of specimens in 1 M HCl and 0.5 M H_2SO_4 with and without addition of different concentrations of inhibitor after 1 h of immersion period at 25°C was determined. The average three triplicate values was used according to the ASTM standard procedure described in literature[11].

The electrochemical measurements were carried out in a conventional three electrode cylindrical pyrex glass cell. The solution volume was 100 cm^3. The iron specimen of 1 cm^2 area was embedded in teflon and used as working electrode. A saturated calomel electrode (SCE) and a platinum electrode were used, respectively as reference and auxiliary electrodes. The electrochemical impedance experiments were carried out at E_∞ after 30 min immersion of the specimen in acid solution at frequency range from 100 kHz to 100 mHz with sine wave voltages of 5 mV peak to peak. The polarization curves were recorded at a scan rate of 1 mV/sec, after 30 min immersion from –800 to –100 mV *vs.* SCE. The electrochemical experiments were carried out with a potentiostat/galvanostat 263A (EG&G) Princeton applied research HF response model 1025.

RESULTS AND DISCUSSION

Gravimetric measurements: From the experimental data, inhibition efficiency ($\eta_w\%$) was determined in 1 M HCl and 0.5 M H_2SO_4 at 25°C after 1 h immersion as follows[12]

$$\eta_w\% = \frac{w_0 - w}{w_0} \times 100 \tag{1}$$

where w_0 and w are the values of weight loss of mild steel after immersion in solution without and with inhibitor respectively. The data are summarized in Table-1.

TABLE-1
INHIBITION EFFICIENCIES FOR DIFFERENT CONCENTRATIONS OF INHIBITOR FOR THE CORROSION OF MILD STEEL IN 1.0 M HCl AND 0.5 M H_2SO_4 OBTAINED FROM WEIGHT LOSS MEASUREMENT

Conc. (ppm) of **A1** compound	Inhibition efficiency ($\eta\%$)	
	1.0 M HCl	0.5 M H_2SO_4
25	75	72.5
50	89	77.5
75	91	85.5
100	97	95.2

With increasing inhibitor concentration, the inhibition efficiency increases. It is observed that the inhibition efficiency in 1.0 M HCl is comparatively higher than that in 0.5 M H_2SO_4 solutions.

Electrochemical impedance spectroscopy (EIS): Fig. 2 presents Nyquist plots of mild steel in inhibited and uninhibited acidic solutions (1.0 M HCl and 0.5 M H_2SO_4) containing various concentrations of (A1). The charge transfer resistance (R_{ct}) values are calculated from the difference in impedance at lower and higher frequencies[13]. The double layer capacitance (C_{dl}) was obtained from the follow equation[12]

$$F(-z''_{max}) = \frac{1}{2\pi C_{dl} R_{ct}} \qquad (2)$$

F is the frequency at the apex of the semicircle in the Nyquist plot.

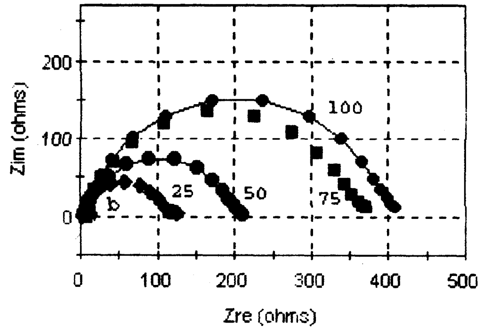


Fig. 2. Nyquist plots for mild steel in 1.0 M HCl in the presence of various concentrations of inhibitor (A1).

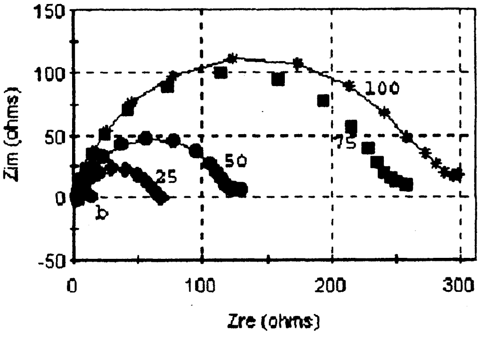


Fig. 3. Nyquist plots for mild steel in 0.5 M H_2SO_4 in the presence of various concentrations of inhibitor (A1).

The inhibition efficiency η (%) of inhibitor is calculated by the equation[14]

$$\eta\% = \frac{R_{ct} - R_{0ct}}{R_{ct}} \times 100 \qquad (3)$$

where R_{ct} and R_{0ct} are the charge transfer resistance values with and without inhibitor, respectively. The impedance parameters derived from Nyquist plots are summarized in Tables 2 and 3.

TABLE-2
IMPEDANCE PARAMETERS AND INHIBITION EFFICIENCY FOR MILD STEEL IN 1.0 M HCl CONTAINING DIFFERENT CONCENTRATIONS OF INHIBITOR (A1)

Conc. (ppm) of **A1** compound	R_{ct} (Ω cm^2)	C_{dl} (μF cm^{-2})	η (%)
Blank	12.8	1064	—
25	123	311	89.8
50	205	183	93.8
75	363	162	96.5
100	402	145	96.8

TABLE-3
IMPEDANCE PARAMETERS AND INHIBITION EFFICIENCY FOR MILD STEEL IN 0.5 M H_2SO_4 CONTAINING DIFFERENT CONCENTRATIONS OF INHIBITOR (A1)

Conc. (ppm) of **A1** compound	R_{ct} (Ω cm^2)	C_{dl} (μF cm^{-2})	η (%)
Blank	1822	649	—
25	65	359	83
50	127	291.5	91
75	255.5	219	95
100	296	198	96.1

It is found from the diameter of semicircles, as inhibitor concentration increases C_{dl} values tend to decrease, R_{ct} values increase. It is due to the adsorption of inhibitor on the metal surface and leads to protective film formation[15]. Similar behaviour is observed in both acidic media. The efficiency in 0.5 M H_2SO_4 is comparatively lower than in 1.0 M HCl solution. It is similar to the result observed from weight loss.

Tafel polarization curves: Figs. 4 and 5 show the potentiokinetic polarization curves of mild steel in both acid (1.0 M HCl and 0.5 M H_2SO_4) at various concentrations of inhibitor (**A1**). The different electrochemical parameters and corrosion inhibition efficiency (η%) derived from these curves are given in Table-4. The inhibition efficiency is defined as follows[4].

$$\eta\% = \frac{I_0 - I}{I_0} \times 100 \qquad (4)$$

where I_0 and I are the uninhibited and inhibited corrosion current densities determined by extrapolation of cathodic and anodic tafel lines at points 120 mV more positive and negative than $E_{corr.}$

The results of Fig. 4 and Fig. 5 indicate that **A1** inhibitor has both cathodic and anodic inhibition effects in both 0.M HCl and 1.0 M H_2SO_4 media.

The relationship between η (%) and the immersion time for one concentration of **A1** (75 ppm) is shown in Fig. 6 by using Tafel polarization curves. It is found that the I_{corr} values for mild steel in 1 M HCl without **A1** (blank) increase with the immersion time, whereas the I_{corr} values for mild steel in acid with the inhibitor

(A1) decrease with the immersion time to 60 min and after that the values of I_{corr} are constant. Similar behaviour was observed in 0.5 M H_2SO_4. The change in I_{corr} values in presence of inhibitor is due to the adsorption of the organic molecules on the metal surface and decrease in the extent of dissolution reaction.

TABLE-4

TAFEL POLARIZATION PARAMETER VALUES FOR THE CORROSION OF MILD STEEL IN 1.0 M HCl AND 0.5 M H_2SO_4 CONTAINING DIFFERENT CONCENTRATIONS OF SCHIFF-BASE COMPOUND (A1)

Solutions	Conc. of A1 (ppm)	E_{corr} vs. SCE (mv)	I_{corr} (μ A cm^{-2})	η (%)
HCl	0	–497	1218	—
	25	-506	195.5	84
	50	–498	98	92
	75	–491	94.5	92.3
	100	–497	54	95.6
H_2SO_4	0	-508	1971	—
	25	–499	327.5	83.4
	50	–499	185	90.6
	75	–498	140	93
	100	–497	111	94.3

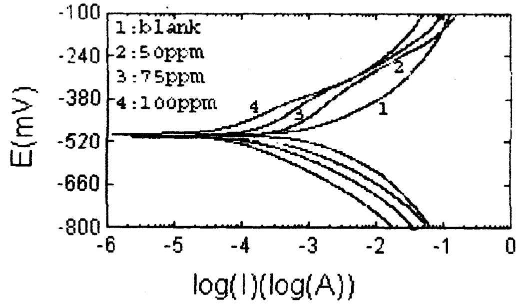


Fig. 4. The polarization curves for mild steel in 1 M HCl with various concentrations of Schiff-base compound (A1)

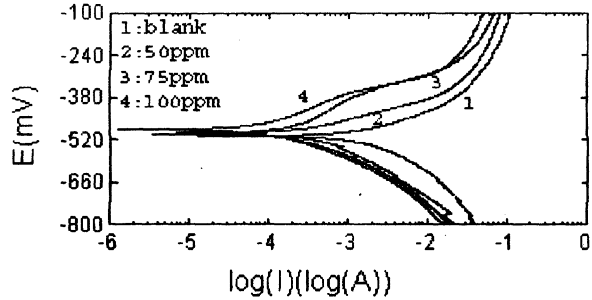


Fig. 5. The polarization curves for mild steel in 0.5 M H_2SO_4 with various concentrations of Schiff-base compound (A1)

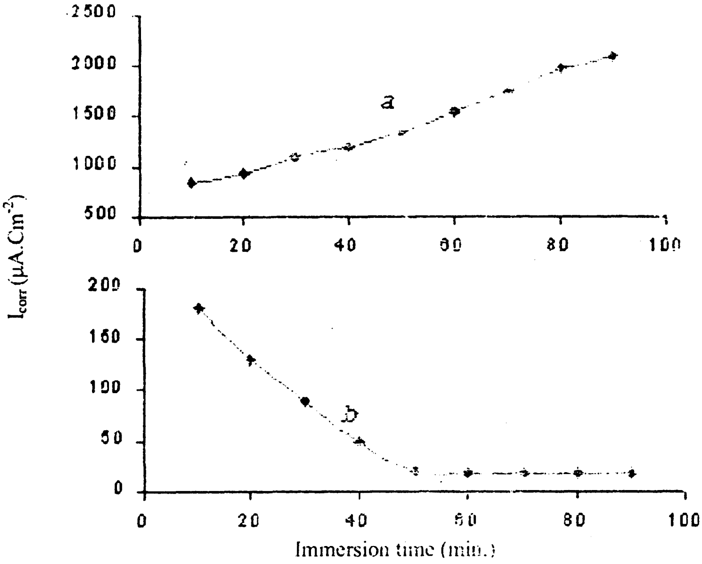


Fig. 6. Relation between I_{corr} and immersion time for mild steel in 1 M HCl (a) and 1.0 M HCl + 75 ppm Schiff-base compound (b)

It can be concluded from Fig. 7 (1 and 2) that inhibition efficiencies obtained from weight loss, electrochemical impedance spectroscopy measurements and polarization curves are in good agreement.

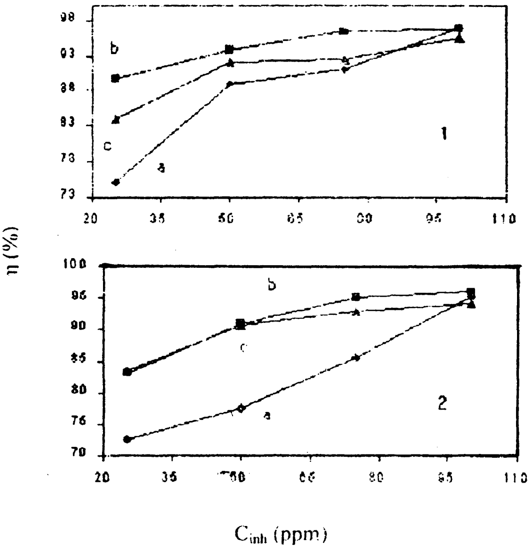


Fig. 7. Inhibition efficiency for mild steel in 1 M HCl (1) and 0.5 M H_2SO_4 (2) containing different concentration of A1 (a). Weight loss measurement, (b). The charge transfer resistance and (c). Polarization curves.

Adsorption isotherm: The two main types of adsorption of an organic inhibitor on a metal surface are physical and chemical. Physical adsorption is due to the electrostatic attraction between the inhibiting ions or dipoles and the electrically charged surface of the metal. The forces in electrostatic adsorption are generally weak. The inhibiting species adsorbed on the metal due to electrostatic forces can also be desorbed easily.

Chemisorption is probably the most important type of interaction between the metal surfaces and an inhibitor molecule. The adsorbed species is in contact with the metal surface. A coordinate type of bond involving electron transfer from inhibitor to the metal is assumed to take place in the process. The chemisorption process is slower than electrostatic (physical) sorption and has higher activation energy. In general the organic inhibitors used have reactive functional groups, which are the sites for the chemisorption process. The strength of the adsorption bond depends on the electron density on the donor atom of the functioned group and the polarizability of the group[1]. The degree of surface coverage by the adsorbed inhibitor was obtained using the following equation[16]:

$$\theta = \frac{I_0 - I}{I_0 - I_m} \qquad (5)$$

where I_m is the corrosion current at maximum efficiency. If the plots of **A1** concentration *vs.* the $C_{inh}\theta^{-1}$ are linear, it confirms that the adsorption is Langmuir type (Figs. 8a and 8b).

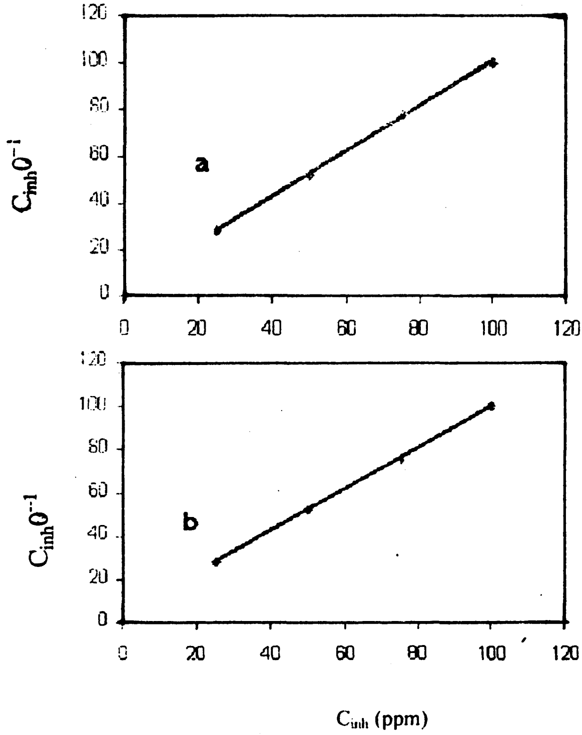
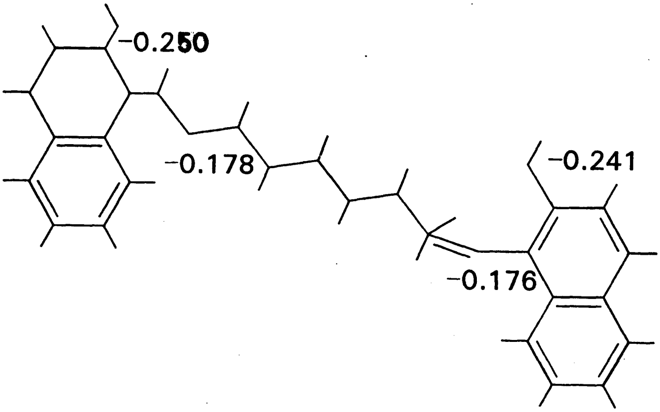


Fig. 8. Langmuir adsorption plots for mild steel in 1 M HCl: (a) 0.5 M H_2SO_4 (b) containing various concentrations of (A1)

Theoretical studies: In continuation, we have further studied some properties for the molecular structure of **A1** tetradentate Schiff base compound. All calculations were performed using AM1 semiempirical method at high precision.

So the geometrical variables (bond lengths, bond angles, point group, heat of formation and the energy level for all molecular orbital) were calculated. The calculated atomic net charges for **A1** are shown in Fig. 9.



The net charges on N and O coordination sites are shown. This Schiff-base ligand has a very active coordination site, so it adsorbs by mild steel surface. Some of calculated data for Schiff-base ligand **(A1)** are summarized in Table-5.

Table-5 indicates that the **A1** compound is a good N(2), O(2)-coordination ligand because the coordination sites, O(1), O(2), N(3) and N(4) atoms have negative net charges.

TABLE 5
SOME OF CALCULATED PROPERTIES FOR A1 COMPOUND BY AM1 SEMIEMPIRICAL METHOD

Compound	Dipole moment (μ debye)	Coordination sites net charge	P.G.	Heat of formation (kcal/mol)
Al	2.809	O(1) –0.240 O(2) –0.250 N(3) –0.178 N(4) –0.176	Cl	13.6788

Conclusion

1. The new synthetic Schiff-base **(A1)** is a good inhibitor in both acids, but the better performance was seen in the case of 1.0 M HCl.
2. Tafel polarization curves indicate that **A1** compound has a mixed anodic-cathodic nature.
3. Tafel lines shape in all of cathodic curves indicate that the mechanisms of hydrogen evolution reaction at the mild steel surface are the same.

4. The inhibition efficiency of **A1** increases with its concentration and reaches a maximum at 100 ppm in both acid solutions.
5. The adsorption of **A1** on the mild steel surface in both acids obeys a Langmuir adsorption isotherm.
6. The efficiency from various techniques is in good agreement.
7. Theoretical data are in good agreement with experimental data.

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